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FROM GAS-PHASE OXIDATION TO NANOPARTICLES
– A MASS SPECTROMETRIC APPROACH

NINA SARNELA

Institute for Atmospheric and Earth System Research / Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

Academic dissertation

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Author's Address: Institute for Atmospheric and Earth System Research / Physics
P.O. Box 64
FI-00014 University of Helsinki
nina.sarnela@helsinki.fi

Supervisors: Associate Professor Mikko Sipilä, Ph.D.
Institute for Atmospheric and Earth System Research / Physics
University of Helsinki

Professor Tuukka Petäjä, Ph.D.
Institute for Atmospheric and Earth System Research / Physics
University of Helsinki

Academician, Academy Professor Markku Kulmala, Ph.D.
Institute for Atmospheric and Earth System Research / Physics
University of Helsinki

Reviewers: Research Professor Hannele Hakola, Ph.D.
Finnish Meteorological Institute, Helsinki, Finland

Heikki Lihavainen, Ph.D.
Svalbard Integrated Arctic Earth Observing System (Director),
Longyearbyen, Norway
Finnish Meteorological Institute (Research Professor), Helsinki,
Finland

Opponent: Associate Professor Marianne Glasius, Ph.D.
Department of Chemistry
University of Aarhus

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From gas-phase oxidation to nanoparticles – a mass spectrometric approach

Nina Matilda Sarnela

University of Helsinki, 2019

Abstract

Atmospheric aerosols are small liquid or solid particles suspended in the air. These small particles have significant effects to our climate and health. Approximately half of the particles that grow into cloud condensation nuclei –size are primary particles and emitted directly into the atmosphere, whereas the other half are secondary particles which are formed in the atmosphere. In new particle formation, molecular clusters form from atmospheric low-volatility vapors by condensation and/or chemical reactions.

Atmospheric oxidation is a key phenomenon enhancing atmospheric particle formation since oxidized compounds condense easier due to their lower vapor pressure. So far two oxidation processes have been identified as relevant for new particle formation: the oxidation of sulfur dioxide to sulfuric acid and oxidation of volatile organic compounds to highly oxygenated compounds. The most significant atmospheric oxidants have previously thought to be ozone, hydroxyl radical and nitrate radical. Recently the importance of stabilized Criegee intermediates in atmospheric oxidation has been brought into discussion.

In this thesis, we used Chemical Ionization Atmospheric Pressure interface Time of Flight mass spectrometer together with different particle measurements in order to widen the understanding of the first steps of new particle formation. We also developed new mass spectrometric measurement techniques to fill the gaps in our current methods. We developed an indirect method to measure non-OH oxidants of sulfur dioxide to better understand the role of stabilized Criegee intermediates and other non-OH oxidants of sulfur dioxide in sulfuric acid formation. We also developed a new technique to determine concentration of ambient dimethylamine at sub-pptV-level. We used both of these new techniques to measure the ambient concentrations in Boreal forest, at SMEAR II station (Station for Measuring Ecosystem-Atmosphere Relations II, Hyytiälä, Finland).

Furthermore, we measured new particle formation in different environments and in a chamber study and tried to identify the condensing vapors. We studied the ozonolysis of α -pinene, the most abundant monoterpene in the atmosphere, in controlled chamber measurements in order to be able to follow the formation of highly oxygenated organics and oxidation of sulfur dioxide purely by stabilized Criegee intermediates and compare the results with kinetic model results. We studied the new particle formation near an oil refinery and found that significantly large fraction of the growth during the new particle formation events was due to sulfuric acid condensation. In our studies at the Atlantic coast, we identified the molecular steps involved in new particle formation at iodine-rich environment and could follow the growth of molecular clusters by subsequent addition of iodic acid molecules. We also did field measurements in Arctic and Antarctic sites and showed that the occurrence of high iodic acid concentration is not limited only to coastal areas with macro algae beds.

Keywords: mass spectrometry, atmospheric aerosols, low-volatility vapors, ozonolysis, new particle formation

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List of publications

This thesis consists of an introductory review, followed by five research articles. In the introductory part, the papers are cited according to their roman numerals. Paper I is reprinted with permission of Boreal Environment Research Publishing Board. Papers II and III are reprinted under the Creative Commons Attribution 4.0 International licence. Paper IV is reprinted under the CC-BY-NC-ND 4.0 license. Paper V is reprinted with a permission from Nature Research.

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List of abbreviations

APi-TOF	atmospheric pressure interface time of flight mass spectrometer
BA	butylamine
CCN	cloud condensation nuclei
CI	chemical ionization
CLOUD	cosmic leaving outdoor droplets experiment in CERN
CPC	condensation particle counter
DEA	diethylamine
DMA	dimethylamine
DMPS	differential mobility particle sizer
EA	ethylamine
FR	flow reactor
HOM	highly oxygenated organic compound
HR-DMA	high resolution differential mobility analyzer
lpm	liters per minute
MA	methylamine
MCP	multi-channel plate
mlpm	milliliters per minute
NAIS	neutral cluster and air ion spectrometer
PA	propylamine
ppqV	parts per quadrillion in volume
pptV	part per trillion in volume
PSM	particle size magnifier
SA	sulfuric acid
sCI	stabilized Criegee Intermediate
SMEAR	Station for measuring ecosystem-atmosphere relations
SMPS	scanning mobility particle sizer
TMA	trimethylamine
VOC	volatile organic compound
X	non-OH oxidants of SO ₂

1 Introduction

Atmospheric aerosols are extremely small (from nanometer to approximately hundred micrometers in diameter) solid or liquid particles suspended in air. In spite of their small size they have significant influence on our everyday life as they affect the air quality and climate on Earth. The impacts of atmospheric aerosols are contradictory. While poor air quality causes negative health effects to humans (Pope and Dockery, 2006), the aerosols have a cooling effect on the climate, thus they can counteract the global warming caused by greenhouse gases (Stocker et al., 2013). Exposure to ambient particulate matter increases morbidity and mortality causing 4.2 million deaths worldwide every year (Cohen et al., 2017) and actions are needed not to increase that number (Apte et al., 2015; Lelieveld et al., 2015).

The balance of Earth's climate depends on the incoming and outgoing energy described by radiative forcing. The greenhouse gases cause positive radiative forcing by absorbing the outgoing long wave radiation and trapping heat in the atmosphere while most of the atmospheric aerosols have the opposite, cooling, effects. Atmospheric particles can directly scatter the incoming solar radiation back to space and indirectly contribute the cooling through clouds and affecting their properties. An exception is black carbon particles that absorb radiation and contribute to the warming of the climate. The current understanding of the radiative forcing of atmospheric aerosols and especially cloud albedo effect has notable uncertainty which affects our ability to estimate how sensitive the climate is to greenhouse gas emissions (Carslaw et al., 2013a, 2013b).

Atmospheric new particle formation starts with a production of small molecular clusters, which can grow further to larger sizes by multicomponent condensation of low-volatile vapors (Kulmala et al., 2013). Depending on the ambient conditions, the particles can grow into larger sizes, decompose or be lost by particle coagulation in which the particles combine into one. When the particles reach diameter size of approximately 50-100 nm, they can act as cloud condensation nuclei (CCN) and have an influence on e.g. the albedo (Twomey, 1974) and lifetime of clouds (Albrecht, 1989) and have other effect on climate and air quality. Model calculations suggest that approximately half of the global CCN of the atmospheric boundary layer and free troposphere are secondary particles meaning that they are formed in the atmosphere from condensable vapors (Merikanto et al., 2009; Gordon et al., 2017). The rest of the CCN particles are primary particles, which means that they are emitted into the atmosphere directly in particle phase, such as desert dust or sea salt.

Recent instrument development has enabled focus on the first steps of particle formation by new particle counters that can detect sub-3nm particles and mass spectrometric methods that can enlighten the composition of these particles and determine the concentration of their precursor vapors. The challenge in measuring the vapors responsible of particle formation and molecular clusters comes from their extremely low concentrations. The air that we breathe contains $2.4 \cdot 10^{19}$ molecules in one cubic centimeter (at 25 °C and 1 atm) of which 99% are nitrogen (N₂) and oxygen (O₂). The vapors participating in the new particle

formation are present as parts per trillion (pptV) or parts per quadrillion (ppqV) volume mixing ratios, which means that we have to find one vapor molecule from a mixture of trillion (10^{12}) or quadrillion (10^{15}) irrelevant molecules. In addition to their low concentration, the precursors of new particle formation are low-volatile, a feature that makes them ready to condense and make molecular clusters, but then again it gets them to stick to any surface they meet, so special care needs to be taken not to lose them all before they are detected. The molecular clusters have even lower concentrations than the vapors and they have tendency to decompose in the mass spectrometer, thus, they are often not detectable. Therefore, we have to rely on simultaneous occurrence of condensable vapors with growing particles and particle growth models. This far the only neutral molecular clusters of which growth have been detected, are sulfuric acid – dimethylamine clusters in the CLOUD chamber measurements (Kürten et al., 2014) and iodine oxide clusters in the atmosphere (**Paper V**). The studies of charged atmospheric particles have identified more chemical identities of molecular clusters: pure organic clusters in chamber studies (Kirkby et al., 2016; Frege et al., 2018;) and sulfuric acid-ammonia clusters in both chamber and field studies (Schobesberger et al., 2015; Jokinen et al., 2018; Yan et al., 2018). However only a small fraction of atmospheric molecules are charged and neutral new particle formation has been found to dominate in the boundary layer (Iida et al., 2006; Kerminen et al., 2010).

Various studies have suggested sulfuric acid as a key compound in new particle formation (e.g. Weber et al., 1997; Wehner et al., 2005; Sihto et al., 2006; Sipilä et al., 2010), however, sulfuric acid alone, or with water, cannot explain the measured atmospheric particle formation rates in the boundary layer (Kirkby et al., 2011). Thus, at least one additional compound is needed to stabilize the sulfuric acid clusters and explain the observed nucleation rates. Atmospherically relevant concentrations of ammonia has been observed to increase the nucleation rates by 100-1000-fold but even this large enhancement is not enough to account for observed boundary layer nucleation in vegetated continents (Kirkby et al., 2011). Only in Antarctica the new particle formation has been observed to be driven solely by ion-induced sulfuric acid-ammonia nucleation (Jokinen et al., 2018). Then again minute, even sub-pptV range, mixing ratios of dimethylamine (DMA), has proven to lead to nucleation rates that could explain atmospheric observations over wide range of sulfuric acid concentrations (Almeida et al., 2013; Kürten et al., 2014). Thus, according to recent chamber experiments, dimethylamine might be an important vapor in atmospheric nucleation but there has not existed techniques to measure the critical sub-pptV concentration range and generally the atmospheric measurements of amines are rare (Ge et al., 2011; Kieloaho et al., 2013; Freshour et al., 2014). Neutral sulfuric acid-dimethylamine clusters have been detected in the chamber measurements (Kürten et al., 2014) but not yet in the ambient atmosphere. Overall, it is challenging to estimate the importance of these bases in the atmospheric particle formation without comprehensive measurements of their concentrations.

Although sulfuric acid has shown to participate in the nucleation in several locations (Weber et al., 1995, 1997; Kuang et al., 2008; Kerminen et al., 2010; Kulmala et al., 2013) its concentration is too low to explain the subsequent growth into large, CCN sized, particles

(Kulmala et al., 1998; Riipinen et al., 2011). Forests and other vegetation emit vast amounts of volatile organic compounds (VOC) into the atmosphere; for instance the most abundant monoterpene, α -pinene, have yearly emissions of 50 Tg (Guenther et al., 1995; Seinfeld and Pankow, 2003). Monoterpenes are a group of biogenic organic compounds with an elemental composition of $C_{10}H_{16}$. α -pinene and other VOC are too volatile to contribute the new particle formation as such but 80% of atmospheric α -pinene undergoes oxidation via ozonolysis (Griffin et al., 1999) and the oxidation yields less volatile organic compounds that can participate in the nucleation and further growth (Ehn et al., 2014; Riccobono et al., 2014; Tröstl et al., 2016).

Field studies in the coastal areas have presented particle formation when high tidal movements expose macro algae beds to sunlight (O'Dowd et al., 2002b; O'Dowd and de Leeuw, 2007). The macro algae emits iodine vapors, mainly I_2 (Huang et al., 2010), that will first photodissociate to I atoms and then rapidly oxidize by atmospheric ozone into different iodine oxides that are potential precursors for new particle formation. During favorable conditions for iodine emissions, a vast amount of small particles have been detected near the emission sites (Berresheim et al., 2002; O'Dowd et al., 2002a) but the exact composition of the nucleating particles had not been resolved before recently (**Paper V**). The occurrence of the iodine oxides have been connected to only certain coastal sites so the global impact of iodine as a precursor of particle formation is still unknown (McFiggans et al., 2010; Mahajan et al., 2011; Atkinson et al., 2012; Lawler et al., 2014; Allan et al., 2015).

Gas-phase oxidation is a crucial process for particle formation. The atmospheric particle precursors are formed from volatile compounds, such as sulfur dioxide SO_2 or different VOC, by oxidation reactions. Sulfuric acid was previously thought to be formed only in hydroxyl radical (OH) oxidation of sulfur dioxide (Lucas and Prinn, 2005) but nowadays the role of stabilized Criegee intermediates (sCI) has been noted (Berndt et al., 2012; Mauldin et al., 2012; Welz et al., 2012). The hydroxyl radical is produced by photolysis of ozone or HONO and in the reaction between hydroperoxyl radical (HO_2) and nitrogen monoxide (NO), so its concentration depends strongly on sunlight. Stabilized Criegee intermediates form in a reaction between unsaturated hydrocarbon, such as VOC, and ozone, thus, its concentration does not have such a strong diurnal dependence. In the reaction of alkene and ozone, first a primary ozonide is formed and then it is decomposed quickly to a carbonyl and a carbonyl oxide known as the Criegee intermediate (Criegee, 1975). A fraction of the Criegee intermediates can be collisionally stabilized (Herron et al., 1982; Donahue et al., 2011) and they are capable of oxidizing sulfur dioxide into sulfuric acid. Several studies propose that sCI can be a significant oxidant in ambient sulfuric acid formation (Mauldin et al., 2012; Welz et al., 2012; Boy et al., 2013; Yao et al., 2014) but lack of direct measurements of sCI concentrations has made it challenging to estimate their importance.

The ozonolysis of alkenes initiate also another crucial reaction pathway: formation of highly oxygenated molecules (HOM; Ehn et al., 2012; Tröstl et al., 2016). The HOM are formed in an autoxidation process where radicals produced after the initial oxidation undergo further oxidation by atmospheric oxygen (Crounse et al., 2013). The pathway starts when organic

radicals, including radicals formed when Criegee intermediates decompose, react with oxygen (O_2) and form a peroxy radical (RO_2). The peroxy radical can go through an intramolecular H-shift, which enables subsequent oxygen addition. The peroxy radical can undergo several additional reactions with atmospheric oxygen or terminate the autoxidation reaction by reaction with NO, HO_2 or another RO_2 and form a closed-shell HOM product (Ehn et al., 2014). This complex reaction pathway can lead to a large amount of different end products from single precursor VOC. In ambient conditions, there are several VOC in the air that can undergo autoxidation, thus, as a result we can observe a large group of highly oxygenated molecules that have ended up with different elemental composition depending on their oxidation level, precursor VOC and terminating agent.

The atmospheric oxidation processes and the molecular clusters studied in this thesis are shown in Figure 1. The aim of this thesis is to widen the understanding of the first steps of new particle formation by using state-of-the-art mass spectrometric methods combined with particle measurements. We measured new particle formation in different environments and in a chamber study and identified the condensing vapors and formed molecular clusters. We also filled gaps in our current understanding of atmospheric processes by developing new mass spectrometric measurement methods. In detail, the main objectives of this thesis are:

- 1) To develop new mass spectrometric measurement techniques: i) to measure the concentration of non-OH oxidants of sulfur dioxide to better understand the role of stabilized Criegee intermediates and other non-OH oxidants of sulfur dioxide in sulfuric acid formation (**Paper I**) and ii) to determine the concentration of ambient dimethylamine at sub-pptV-level and map out the possibility to measure other atmospheric amines and ammonia (**Paper II**).
- 2) To investigate the formation of HOM and the oxidation of sulfur dioxide purely by stabilized Criegee intermediates due to the ozonolysis of α -pinene and to quantify the yield of HOM and sCI in controlled chamber conditions (**Paper III**).
- 3) To identify the condensable vapors and molecular cluster formation pathways of new particle formation in different kind of environments (Boreal forest, industrial area, coastal area, and Arctic area) (**Papers I-II and IV-V**).

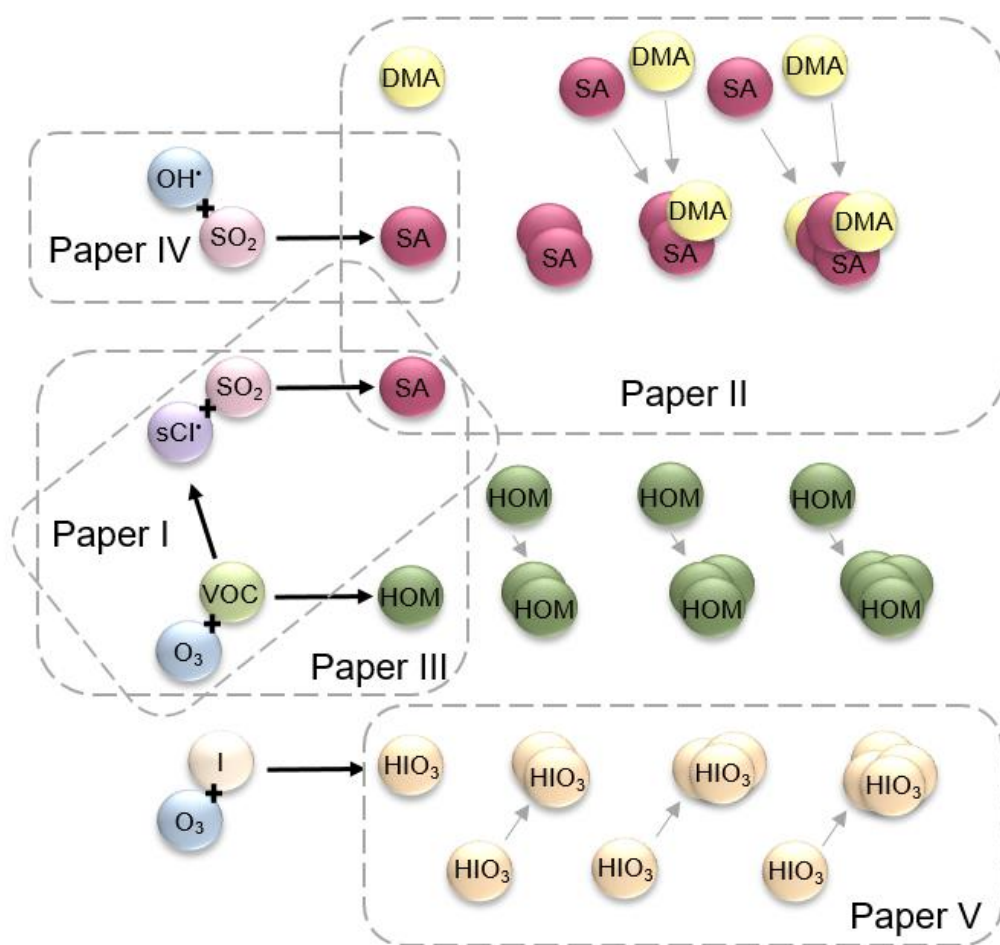


Figure 1. The atmospheric oxidation processes and the molecular clusters studied in this thesis.

2 Experimental methods

2.1 Chemical Ionization Atmospheric Pressure interface Time-of-Flight mass spectrometer (CI-APi-TOF)

The core instrument of this study is Chemical Ionization Atmospheric Pressure interface Time of Flight mass spectrometer (CI-APi-TOF, Jokinen et al., 2012). The instrument can be used with negative or positive polarity and all of the studies of this thesis are done with negative polarity using nitrate ion (NO_3^-) as a reagent ion. The detection of CI-APi-TOF is based on proton transfer reactions or clustering with the nitrate ion through collisions with nitrate ions (NO_3^-), nitrate ion-nitric acid dimers ($\text{HNO}_3\text{NO}_3^-$) and nitrate ion-nitric acid trimers ($(\text{HNO}_3)_2\text{NO}_3^-$). The nitrate ion is a highly selective reagent towards acidic compounds since $\text{HNO}_3\text{NO}_3^-$ is more stable cluster than the ion-molecule clusters of less oxidized sample molecules. The nitrate ion reacts only with strong acids, such as malonic acid, sulfuric acid and methane sulfonic acid (Eisele and Tanner, 1993) and oxidized organic compounds that have at least two hydroperoxy (OOH) groups or other H-bond-donating groups (Hytinen et al., 2015). When studying new particle formation, the acidic compounds are crucial because they are also low-volatility compounds, which makes them prospective participants in formation of molecular clusters.

In chemical ionization inlet (Figure. 2a) around 10 liters per minute (lpm) of sample flow is drawn into the inlet with a $\frac{3}{4}$ " stainless steel tube while around 20 lpm sheath flow is mixed with a ~ 5 milliliters per minute (mlpm) flow of air saturated with the reagent gas (HNO_3). The sheath gas with nitric acid molecules is guided through an ion source where they are ionized to nitrate ions (NO_3^-) with a soft x-ray source (Hamamatsu) or with a radioactive source (^{241}Am). Both of the ionization methods work in the same way: the radioactive source produces α -radiation and soft x-ray source γ -radiation that can detach an electron from nitrogen. When the detached electron meets oxygen, it can produce O_2^- , which is capable of ionizing nitric acid by proton transfer. The formed nitrate ions or their clusters are guided to the sample gas stream by two voltages. The nitrate ions (or ion-clusters) and the molecules of the sample have around 200 ms of time to react with each other in drift tube. The voltage of the wall of the drift tube keeps the ions in the center of the tube and from there they enter the APi-TOF through a 0.3 mm critical orifice with flow of ~ 0.8 lpm.

In the atmospheric pressure interface the molecules of the sample are gradually pumped out while the ions are kept in the middle of the stream by quadrupoles and ion lenses (Figure 2d). In the first quadrupole the pressure is around 2 mbar and in the second one 10^{-2} mbar. In the third chamber the pressure is 10^{-4} mbar and from there the ions are guided to the time of flight (TOF) chamber with pressure of 10^{-6} mbar. In the TOF the ions are accelerated with an energy pulse and they are separated by their time of flight to reach the detector in the chamber. When the ions have equal kinetic energy their velocity (v) depends on their mass to charge ratio (m/z) according to equation 1:

$$v = \sqrt{\frac{2V e}{m/z}} \quad (1)$$

where V is the acceleration voltage and e the elementary charge. The resolution of mass spectrometer is defined as $R=M/\Delta M$ in which M is the mass to charge ratio of the peak and ΔM the width of the peak at its half height. In our instruments the resolution was around 3000 and mass accuracy around 5 ppm.

In the time-of-flight chamber, there are reflectrons on both ends of the chamber so the ions can be guided to fly a V or a W shaped flight path. In all the studies of this thesis, we used the shorter flight path in order to get better transmission for ions but it comes with a consequence of lower resolution. The range of mass to charge ratio measured with APi-TOF can be selected according to the interest of the study. When measuring sulfuric acid and highly oxygenated organics (**Papers I-IV**) we measured mass range 10-1000 m/z and when measuring large molecular clusters (**Paper V**) we measured mass range 10-2500 m/z . In APi-TOF we use two micro-channel plates (MCP) as a detector. The MCP consists of dense array of small channels and each of them work as an electron multiplier. This means that the impact of charged ions on the MCP generates a pulse of electrons, which will consequently collide to the walls of the channels and thus produce cascade of electrons. In this way, the signal of ions is enhanced and finally the total current is measured at the anode. The data is recorded with time-to-digital converter by co-adding spectra for selected time such as 1-5 s. Instrument is pulsed at frequency of 12 kHz, which means 12000 co-additions per second. Even though we can reach very high time resolution with this instrument, in ambient measurements, we often aim for high sensitivity and gather signals over longer period. As a result, when we wanted to identify molecular clusters up to 2200 m/z we averaged the data over two hours while when we followed the appearance of oxidation products in chamber studies we used data averaged over 30 seconds.

The chemical ionization method enables quantitative measurements of low-volatility vapors but it can also complicate the detection because charging probability depends on the chemical composition of the compound and some compounds of interest may perhaps not be charged (Kurtén et al., 2011). APi-TOF can also be used by itself, without the chemical ionization inlet, to measure the ambient ions in the atmosphere (Ehn et al., 2010a; Junninen et al., 2010). In that case, just a make-up flow is used to bring the sample air to the critical orifice. Only a small fraction of gas phase molecules in the atmosphere are charged and the charge is transferred to energetically favorable direction via frequent collisions of molecules and ions. This means that molecules with the lowest proton affinity, such as strong acids, will end up with negative charge. The ambient ion measurements can give more insight into the processes and molecular clusters in the atmosphere and reflects the behavior of neutral molecules in the atmosphere but the measurements are not quantitative. Concurrent studies with mobility spectrometers and APi-TOF has shown that the instruments agreed well in the mass range 200-1500 Da but below 200 Da the discrepancy was higher probably due to diffusion in mobility measurements or fragmentation/evaporation in mass spectrometry measurements (Ehn et al., 2011).

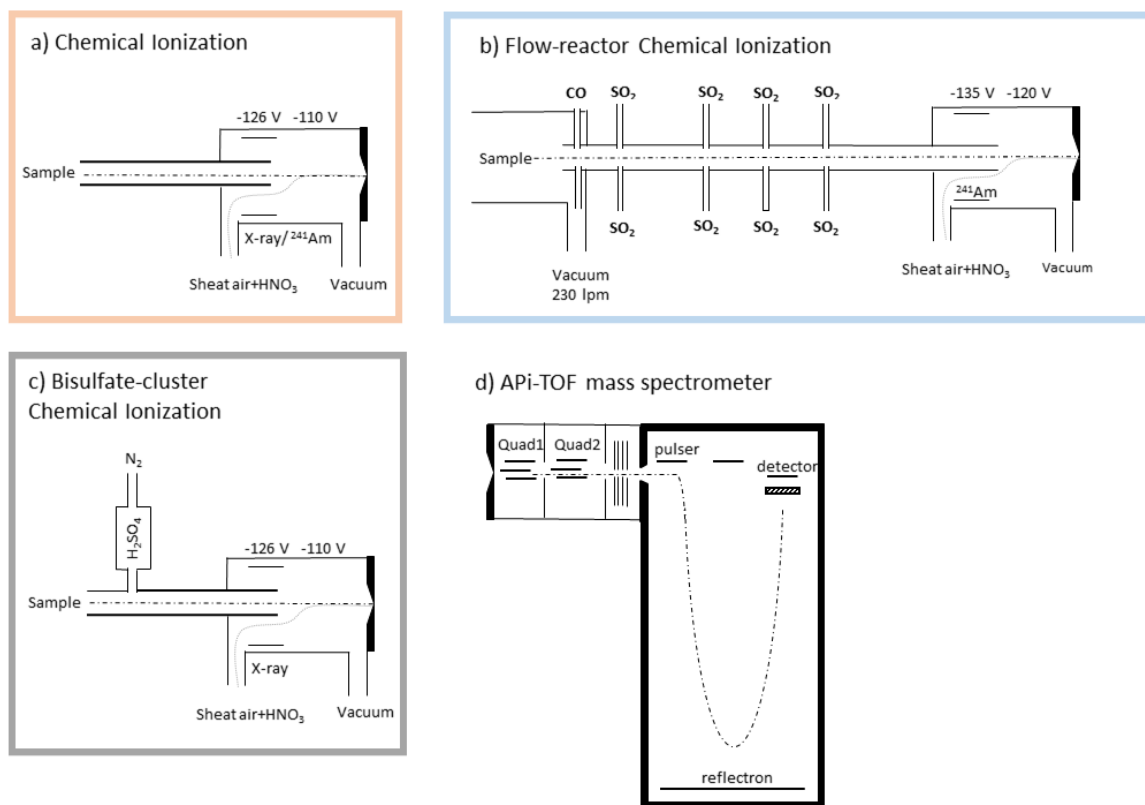


Figure 2. Schematic of the instrumentation used in this thesis: (a) Chemical ionization inlet used in **Papers III-V**, (b) Flow reactor chemical ionization inlet developed in **Paper I**, (c) bisulfate cluster chemical ionization inlet developed in **Paper II** and (d) the atmospheric pressure interface time-of-flight mass spectrometer used in all the studies.

2.2 FR-CI-API-TOF

In **Paper I** we developed a field-deployable instrument, named Flow Reactor CI-API-TOF (FR-CI-API-TOF, Figure 2b) to determine the concentration of stabilized Criegee intermediates and possible other non-OH oxidants of SO₂ such as peroxy radicals (Sander and Watson, 1981; Kurtén et al., 2007). The method cannot distinguish between different oxidants but it measures all the non-OH oxidants of SO₂ as a sum. We used otherwise similar chemical ionization inlet than in Figure 2a but we replaced the sample tube with a flow reactor. When the sample enters the flow reactor, the ambient OH is scavenged by CO that is injected into the flow reactor. Then we inject an excess of SO₂ to the flow reactor consecutively through four different positions and corresponding amount of SO₂ is converted into sulfuric acid by non-OH oxidants of SO₂ (here stated as X). Finally the sulfuric acid concentration is measured by CI-API-TOF and the measured concentration depends on three components: (1) product of the production rate of X in the flow reactor

after the SO₂ injection (PR_X) and X-SO₂ reaction time (t_r), (2) ambient concentration of X ($[X]_{amb}$) and (3) ambient concentration of sulfuric acid ($[H_2SO_4]_{amb}$) at the entrance of the flow reactor (Eq. 2).

$$[H_2SO_4] = PR_X t_r + [X]_{amb} + [H_2SO_4]_{amb}, \quad (2)$$

Berndt *et al.* (2012) used a similar method in laboratory experiments and in their study they took into account also the effects of sCI losses due to flow reactor walls, thermal decomposition and reactions with water vapor. However, using these loss parameters derived from well-defined laboratory experiments did not produce meaningful results in our field measurements in the changing environment. In our measurements, we took into account the different wall loss parameters depending on the distance from the injector to the chemical ionization part of the inlet when calculating the concentration of sulfuric acid at each step. We used a measurement cycle with four different reaction times and one step without any injection of SO₂ to record the ambient sulfuric acid concentration so that it can be subtracted from the concentration measured during the other steps.

In FR-CI-APi-TOF measurements, each measurement cycle gives the sulfuric acid concentration that has been oxidized by non-OH oxidants as a function of the reaction time. The production rate of X and the ambient concentration of X can be determined by fitting a linear regression to the data points so that the production rate is the slope and the concentration is the intercept (see Eq. 2 and Figure 3).

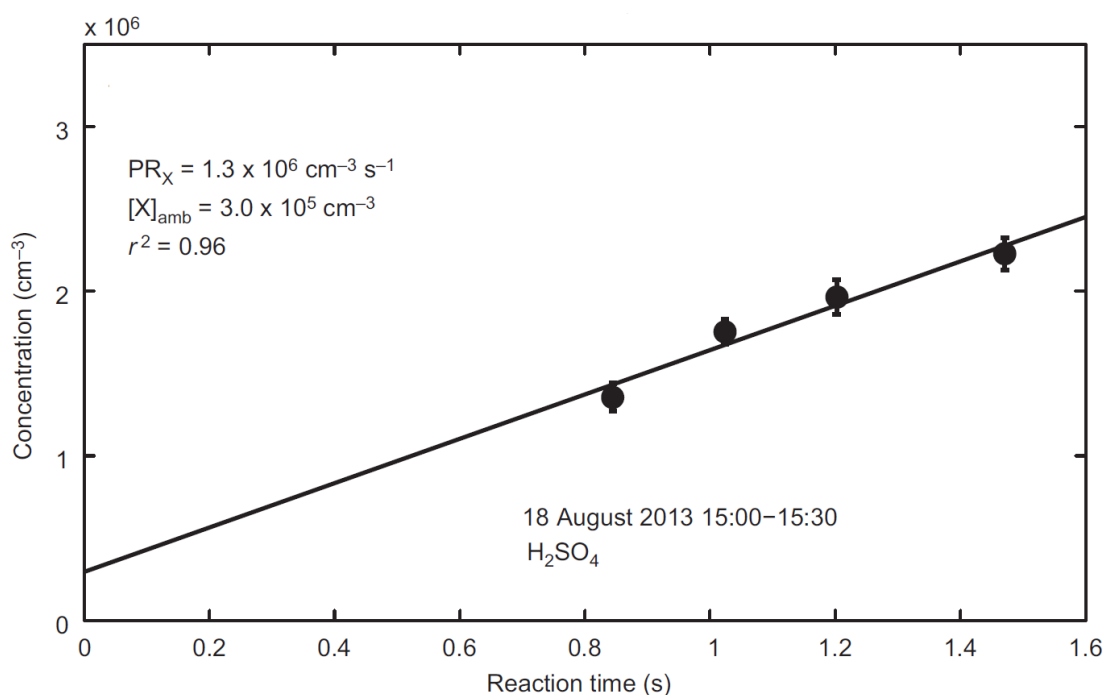


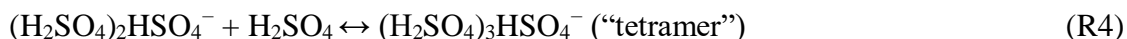
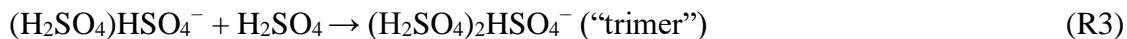
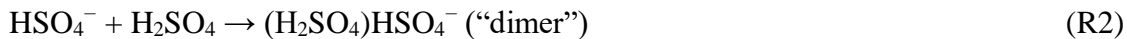
Figure 3. Example of 30 min average of the sulfuric acid concentrations measured in Boreal forest with FR-CI-APi-TOF as a function of the X-SO₂ reaction time. The line shows the linear least square fit to the sulfuric acid concentrations and the error bars represent the 95% confidence intervals. Figure from **Paper I**.

2.3 Bisulfate-cluster CI-APi-TOF

Sulfuric acid clusters with ammonia and dimethyl amine have been detected even with very low base concentrations (pptV-level for ammonia, sub-pptV-level for DMA) in CLOUD chamber studies with atmospherically relevant sulfuric acid concentrations (10^6 - 10^8 molecules per cubic centimeter which means 0.04-4 pptV in mixing ratio), using APi-TOF and CI-APi-TOF (Kirkby et al., 2011; Almeida et al., 2013; Bianchi et al., 2014; Kürten et al., 2014). This observation led to the development of bisulfate-cluster CI-APi-TOF (**Paper II**, Figure 2c). In bisulfate-cluster CI-APi-TOF we feed sulfuric acid into the sample tube of chemical ionization inlet in order to detect atmospheric bases as molecular clusters with sulfuric acid. The sulfuric acid vapor is fed to the sample tube 20 cm before the sample enters the drift tube so that it will get mixed with the bases in the sample before the ionization. We inject the sulfuric acid vapor from a temperature controlled rotating coaxial saturator with a carrier flow of 1-2 litres per minute. This design enables less wall effects because the walls are constantly wet by liquid sulfuric acid. First, we did measurements using nitrogen (bottled, purity 5.0) as the carrier gas for sulfuric acid and dried compressed air filtered with amine-specific gas filter as the sheath gas. This still caused a high background for both ammonia and amines and we changed our sheath gas and carrier gas

into cryogenic nitrogen. This improvement decreased the background significantly but at the same time, it increased the operational costs of using this instrument.

In more detail, the operation of the bisulfate-cluster-CI-API-TOF is based on chemical ionization of sulfuric acid (H_2SO_4) by nitrate ions to form bisulfate ions (HSO_4^- , R1) and subsequent formation of bisulfate ion-sulfuric acid clusters ($(\text{H}_2\text{SO}_4)_n\text{HSO}_4^-$, R2-R4).



In the presence of dimethylamine ($\text{C}_2\text{H}_7\text{N}$), molecular clusters can form when neutral dimethylamine makes an adduct with sulfuric acid cluster or when ambient sulfuric acid – dimethylamine cluster combines with sulfuric acid cluster (R5-R7).



Based on binding energy calculations, ammonia can make a molecular cluster with a sulfuric acid tetramer (R8).



These molecular clusters can also decompose by evaporation, especially in reduced pressure of the Atmospheric Pressure interface. Sulfuric acid dimer, trimer and sulfuric acid trimer clusters with dimethylamine have highly negative formation free energies so the clusters should be virtually non-evaporating in the chemical ionization system with 0.2s residence time (Ortega et al., 2008, 2014). In addition, the sulfuric acid tetramer with dimethylamine should be stable in the CI-inlet at 25°C. The stability of sulfuric acid tetramer and tetramer with ammonia (R4 and R8) is not as high as the sulfuric acid dimethylamine clusters and precise temperature control of the instrument would be needed.

We can get an overview of the cluster formation preferences of bases by studying the signal observed when high concentration of sulfuric acid is mixed with laboratory indoor air (Figure 4.). With our instrument, we can detect dimethylamine (DMA) or ethylamine (EA) and diethylamine (DEA) or butylamine (BA) approximately as abundantly as clusters with sulfuric acid trimer and tetramer. Ammonia, methylamine (MA) and trimethylamine (TMA) or propylamine (PA) can be detected only with sulfuric acid tetramer or larger sulfuric acid clusters. Because the sulfuric acid trimer concentration in our system is significantly higher than the concentration of larger sulfuric acid clusters, we can expect that our sensitivity is greater for bases that can cluster also with sulfuric acid trimer. There are several amines that have the same elemental composition (DMA/EA: $\text{C}_2\text{H}_7\text{N}$, TMA/PA: $\text{C}_3\text{H}_9\text{N}$ and DEA/BA: $\text{C}_4\text{H}_{11}\text{N}$) so we cannot separate them from each other with our method.

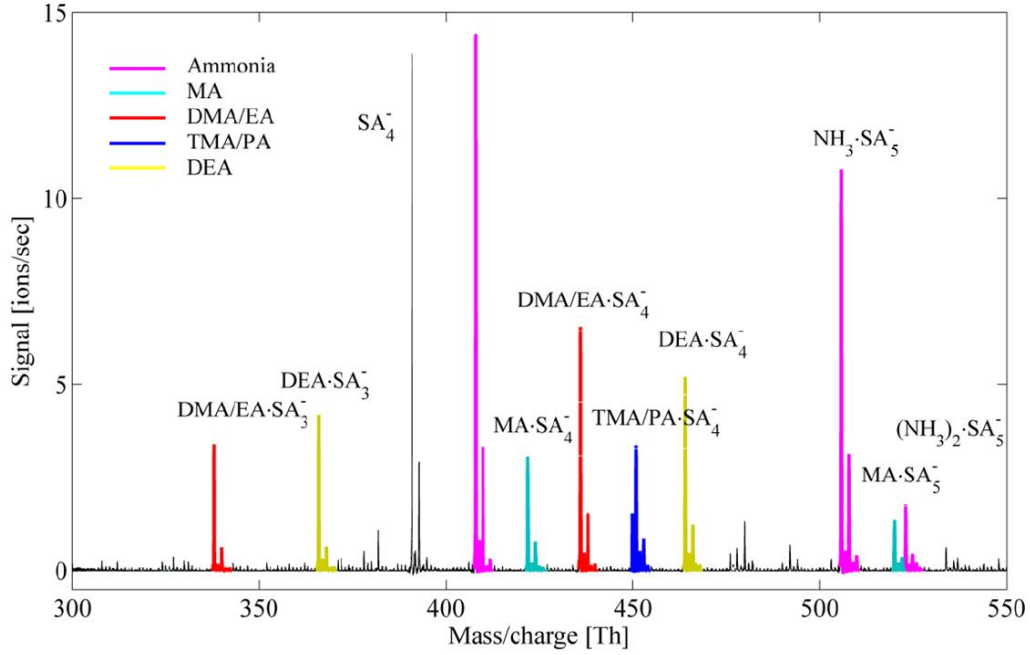


Figure 4. Mass spectrum of the cluster composition when measuring laboratory air mixed with high concentration of sulfuric acid (SA). Figure from **Paper III** (error in the label of $\text{NH}_3\cdot\text{SA}_5^-$ corrected)

2.4 Calculating the concentrations of condensable vapors in the atmosphere

The detection of vapors and clusters in CI-API-TOF depends on their proton affinity, ability of clustering with nitrate ion, transmission and decomposition in the system. For quantitative measurements the instrument needs to be calibrated with the compound of interest. Unfortunately production of well-known concentration of these low-volatility vapors or clusters is not straightforward. The sulfuric acid detection is calibrated by producing sulfuric acid by OH-oxidation and modelling the concentration in the system (Kürten et al., 2012). From the calibration we obtain a calibration constant (c) and the sulfuric acid concentration can be calculated as shown in Eq. 3:

$$[\text{H}_2\text{SO}_4] = \frac{\text{HSO}_4^- + (\text{HNO}_3)\text{HSO}_4^-}{\text{NO}_3^- + (\text{HNO}_3)\text{NO}_3^- + (\text{HNO}_3)_2\text{NO}_3^-} \times c \quad . \quad (3)$$

In the presence of stabilizing agents of sulfuric acid clusters, also the sulfuric acid clusters need to be taken into account when calculating the total concentration of sulfuric acid (Rondo et al., 2016). In the studies of this thesis, we did not have so high concentrations of stabilizing agents that significant amount of sulfuric acid concentration would have been found in the clusters.

Since the sCI concentration was measured indirectly by measuring the produced sulfuric acid, also the FR-CI-API-TOF instrument was calibrated by the same method (**Paper I**). The bisulfate-cluster-CI-API-TOF was calibrated by injecting a known amount of dimethylamine or ammonia to the CLOUD chamber and measuring it with the instrument

(**Paper II**). There has not yet been developed a method to produce HOM or iodic acid in such a controlled manner so that a direct calibration could be done. Thus, their concentration estimates rely on the sulfuric acid calibration with additional correction terms and transmission calibration (Eq.4).

$$[M] = \frac{k_{SA}}{k_M} \times \frac{T_{SA}}{T_M} \times \frac{e_{SA}}{e_M} \times \frac{\sum product\ ion\ signals}{NO_3^- + (HNO_3)NO_3^- + (HNO_3)_2NO_3^-} \times c \quad (4)$$

In the equation 4. $[M]$ is the concentration of interest, c is the calibration constant for sulfuric acid, $\sum product\ ion\ signals$ is the sum of clusters and ions in which the studied compound is seen in the mass spectrum. The first correction term, k_{SA}/k_M , corrects for the difference in reaction rate between the studied compound and reagent ions compared to the reaction rate of sulfuric acid and reagent ions. Sulfuric acid has been found to ionize at the collision frequency with the reagent ion. Since the proton affinity of IO_3^- is considerably lower than of NO_3^- we can expect collision limited ionization for iodic acid as well. As nitrate dimer ($HNO_3NO_3^-$) is an extremely stable cluster and there is an excess of nitric acid in the drift tube, it is plausible that other clusters forming with nitrate ion are even more stable than the nitrate dimer. As we can detect a large total signal of HOM-nitrate clusters, we can assume that they are very stable. If we assume that also HOM forms clusters with nitrate at the collision frequency, we can get the lower limit of HOM concentration. If all the collisions in reality did not produce clusters or some of the formed clusters decomposed in the instrument, the real concentration of HOM would be higher than the estimation got in this method. Ehn et al. (2014) calculated collision limited reaction rates of $k_{SA} = (1.5-2.5) \cdot 10^{-9} \text{cm}^3 \text{s}^{-1}$ and $k_{HOM} = (1.5-2.8) \cdot 10^{-9} \text{cm}^3 \text{s}^{-1}$ by using the formulation of Su and Bowers (Su and Bowers, 1973) and assuming some possible structures of HOM. The achieved collision-limited reaction rates are so close to each other that we can approximate the term k_{SA}/k_{HOM} to 1.

The second term, T_{SA}/T_M , describes the differences in transmission of SA and M through the sampling line and the third term, e_{SA}/e_M , describes the difference in transmission inside the mass spectrometer. The size of the molecule or cluster causes differences in transmission in the sampling line, because the diffusivity decreases as the size of the molecule increases. The pinhole, the quadrupole ion guides, the time-of-flight mass spectrometer, and the multichannel plate detector all have mass discrimination effects that are described by e_{SA}/e_M . The total effect of the terms T_{SA}/T_M and e_{SA}/e_M can be determined experimentally with a high resolution differential mobility analyser (HR-DMA; Junninen et al., 2010). In this method selected size range of particles are guided to API-TOF and the transmission is calculated by dividing the signal in mass spectrum by the signal in the electrometer. As a result, we get a transmission curve that is used to calculate correction coefficients for M, if its transmission differs from the transmission of SA.

2.5 Aerosol particle measurements

The particle number size distributions were measured with different particle counters in this work. We measured the total number concentration of the smallest particles or clusters (1.5–3 nm) with Particle Size Magnifier (PSM, Vanhanen et al., 2011, **Papers IV-V**). In PSM the small particles/clusters are grown by supersaturated diethylene glycol into the sizes that Condensation Particle Counter (CPC) can detect them. With PSM we can get close to the particle sizes we can measure with CI-API-TOF. The largest iodine clusters detected with CI-API-TOF were approximately 1.1 nm in electrical equivalent diameter.

The Neutral cluster and Air Ion Spectrometer (NAIS (Mirme and Mirme, 2013)) was used to measure size distribution of neutral and charged clusters and particles between 2.5 and 40 nm (**Paper III**). In **Paper V** we used Air Ion Spectrometer that measured only ion clusters. Larger particles were measured with nano Scanning Mobility Particle Sizer (nano-SMPS 5–80 nm, **Paper III**) or Differential Mobility Particle Sizer (DMPS 6–1000 nm, **Paper IV**).

2.6 Study sites

This thesis includes four field measurements and one chamber measurement (Figure 5.). The **Paper I** and **Paper III** describe ambient measurements from Station for Measuring Ecosystem-Atmosphere Relations II (SMEAR II station, Hyytiälä, Southern Finland, Hari and Kulmala, 2005) which is a rural background site. The measurement station is located in boreal forest, which is dominated by conifers especially Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). SMEAR II has low local particle matter emissions but high biogenic emissions of monoterpenes, such as α -pinene, which makes it an interesting site to study new particle formation (Bäck et al., 2012; Hakola et al., 2012).

The chamber measurements of **Paper II** were conducted in the CLOUD (Cosmic Leaving Outdoor Droplets) chamber at CERN (Geneva, Switzerland; Duplissy et al., 2016; Kirkby et al., 2011). The CLOUD chamber is a stainless steel cylinder with a volume of 26.1 m³ and with a relatively small wall loss rate, which enables studies of particle formation with atmospherically relevant precursor concentrations. In the CLOUD chamber facility experiments can be done with very well controlled conditions and with extremely low concentrations of contaminants. The chamber is filled with synthetic air provided from cryogenic liquid N₂ and O₂ with addition of water to keep the RH at 38% with chosen precursor gases. The effect of ions can be studied in CLOUD chamber by making three different kind of experiments: neutral by removing the ions with a strong electric field, natural ionization by cosmic rays or enhanced ionization by particle beam from the CERN Proton Synchrotron. The experiments in **Paper II** were done in neutral conditions.

The **Paper IV** presents measurements done in Kilpilahti industrial area at Nyby station (Porvoo, Southern Finland) which is located 1.5 km from an oil refinery. The surroundings of the station are diverse; there are an oil refinery, industrial activities, heavy traffic and a

harbor related to those activities but also rural environment with biogenic emissions. The Kilpilahti industrial area is the largest center of oil refinery and chemical industry in the Nordic countries with total yearly emissions of 2600 tons of nitrogen oxides, 5320 tons of sulfur dioxide, 140 tons of particulate matter and 2850 tons of volatile organic compounds (in 2012, Vaskinen and Kanerva, 2016).

The main measurements of **Paper V** were conducted in coastal environment at Mace Head Atmospheric Research Station (west coast of Ireland, O'Dowd et al., 2002a). The area is affected by strong tidal changes and presence of macro algae beds consisting of kelps (different *Laminaria* species) and other brown algae (*Ascophyllum nodosum* and *Fucus vesiculosus*). During day time low tide conditions the marine algae emits high amounts of iodine into the atmosphere and vast amount of nanoparticles can be detected on the site.

In **Paper V** we also presented data from our field campaigns in the Arctic and Antarctica. The Arctic measurements were done at Villum research station in the coast of Northern Greenland (Nguyen et al., 2016). The station is in very remote location in the Greenland's National park, where the nearest town is Longyearbyen on Svalbard (Norway), 720 km east of the station. The Antarctic measurements were done at the Aboa research station in Queen Maud Land (Asmi et al., 2010). Aboa research station is further away from the coast (130 km) and the air masses entering the station do not travel often straight from the coast side.

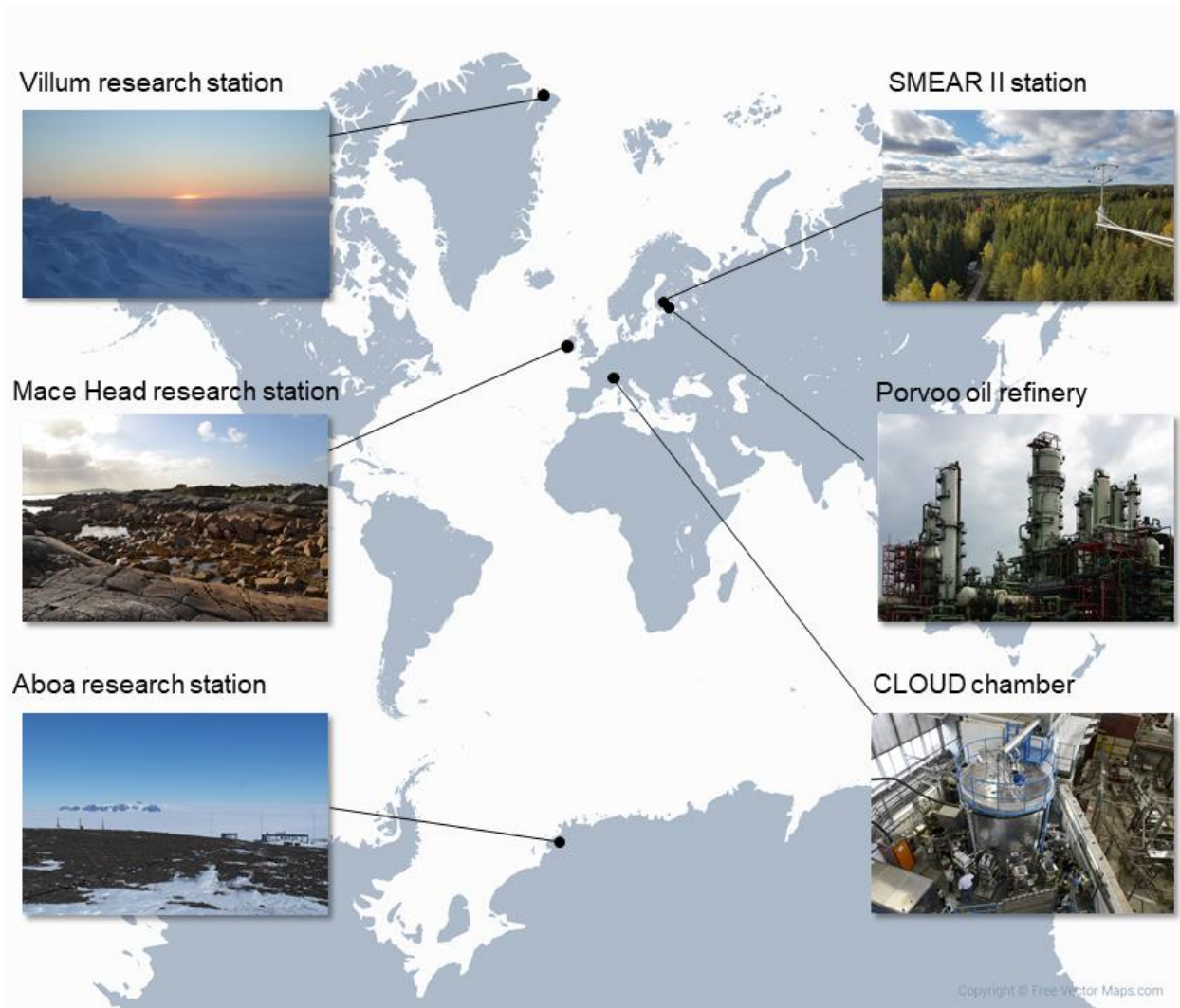


Figure 5. The study sites of this thesis. Pictures from Villum research station, Hyytiälä SMEAR II station, Mace Head research station, Porvoo oil refinery and CLOUD chamber: Nina Sarnela, Aboa research station: Tuija Jokinen.

3 Ozonolysis of α -pinene in the CLOUD chamber and model comparison

In the CLOUD chamber measurements, we tried to mimic the particle formation in the atmosphere by providing similar conditions that have been observed in field measurements. Compared to other α -pinene ozonolysis experiments done elsewhere (eg. Ehn et al., 2014; Jokinen et al., 2015), the CLOUD chamber provides smaller wall loss rate. In CLOUD chamber the loss rate of sulfuric acid is around $1.8 \cdot 10^{-3} \text{ s}^{-1}$, which is similar to the condensation sink in relatively unpolluted ambient environments, such as SMEAR II station. The condensation sink is a term that describes how rapidly molecules will condense onto pre-existing aerosols and it depends on the shape and concentration of the size distribution. In our experiments, we tried to mimic the night time conditions of Boreal forest (SMEAR II station) therefore we used α -pinene and SO_2 as precursor vapors and added an atmospherically relevant concentration of ozone into the chamber. At the same time, we removed the day time oxidant, OH radical, by injecting H_2 into the chamber. The temperature was kept at 278 K and all the ions were removed with high voltages in order to follow neutral particle formation.

In the beginning of the α -pinene ozonolysis experiments, we injected α -pinene to the chamber that has constant ozone, sulfur dioxide and hydrogen concentration and we observed immediate sulfuric acid and highly oxygenated molecule formation (Figure 6). The particle growth above 3 nm measured by NAIS followed approximately 45 minutes after the injection. During those 45 minutes the condensing vapor concentrations increased and molecular clusters started to form. As the concentration of α -pinene continued to increase and the particles grew into larger sizes the condensable vapors reached their steady-state concentrations relatively fast, sulfuric acid slightly before the HOM due to its faster wall loss rate.

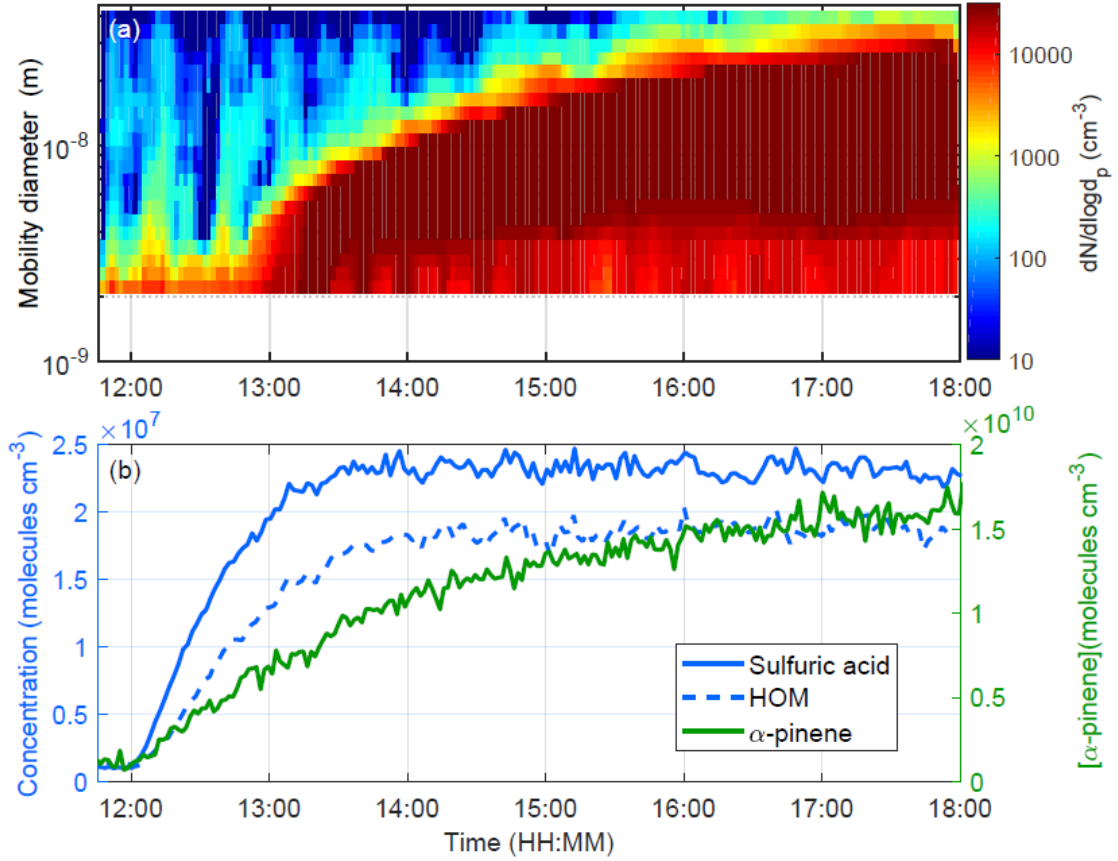


Figure 6. Example of α -pinene ozonolysis experiment in the CLOUD chamber. a) The size distribution 2-40 nm measured by NAIS b) Concentrations of sulfuric acid, HOM and α -pinene.

We used kinetic models to simulate the formation of stabilized Criegee Intermediates (sCI), Highly Oxygenated Molecules (HOM) and sulfuric acid concentrations in the CLOUD chamber. The production of sCI was calculated by using the measured concentrations of ozone and α -pinene and reaction rate coefficient from study of Atkinson et al. (2006). The differential equation describing the evolution of the concentration of stabilized Criegee intermediates in the CLOUD chamber can be written as:

$$\frac{d[sCI]}{dt} = (Y_{sCI} \times k_{O_3+\alpha\text{-pinene}} \times [O_3] \times [\alpha\text{-pinene}]) - (k_{loss} \times [sCI]) - (k_{sCI+SO_2} \times [SO_2] \times [sCI]). \quad (5)$$

In the model we used reaction rate coefficient (k_{sCI+SO_2}), sCI yield term (Y_{sCI}) and loss term (k_{loss}) from the study of Sipilä et al. (2014). Three loss terms were taken into account in the sCI simulation: (1) reaction with sulfur dioxide, (2) thermal decomposition and (3) reaction with water vapor. The latter two are included in the loss term k_{loss} (Eq. 6).

$$k_{loss} = k_{dec.} + (k_{(sCI+H_2O)} \times [H_2O]) \quad (6)$$

The condensation sink, wall loss and dilution are negligible compared to the k_{loss} . Previous studies (Berndt et al., 2014; Huang et al., 2015) have shown that the reaction rate of sCI and water is strongly dependent on the structure of sCI and that sCI with complicated substitution groups react with water slowly but with sulfur dioxide quickly. In the case of α -pinene, or other monoterpene derived sCIs, the relative rate coefficient k_{loss}/k_{sCI+SO_2} was found to be nearly independent of the relative humidity (Sipilä et al., 2014).

The production of sulfuric acid was calculated by using the modelled concentration of sCI, measured concentration of sulfur dioxide and reaction coefficient from study of Sipilä et al. (2014) (Eq. 7). Three loss terms were taken into account in the sulfuric acid simulation: (1) the condensation sink, (2) the wall loss and (3) the dilution in the chamber. The condensation sink due to particles in the chamber was determined from the size distribution measured by nanoSMPS, the wall loss of sulfuric acid is well defined (Duplissy et al., 2016; Rondo et al., 2016) and the dilution rate calculated from the injections of make-up gases into the chamber. Therefore the differential equation describing the development of sulfuric acid concentration is:

$$\frac{d[H_2SO_4]}{dt} = k_{sCI+SO_2} \times [sCI] \times [SO_2] - (CS + k_{wall_loss} + k_{dil}) \times [H_2SO_4]. \quad (7)$$

The production of HOM was calculated with measured ozone and α -pinene concentration, Atkinson's reaction rate coefficient (Atkinson et al., 2006) and an experimentally derived yield term Y_{HOM} (Ehn et al., 2014; Jokinen et al., 2015). The differential equation describing the evolution of HOM concentration is written as:

$$\frac{d[HOM]}{dt} = Y_{HOM} \times k_{O_3+\alpha-pinene} \times [O_3] \times [\alpha-pinene] - (CS + k_{wall_loss} + k_{dil}) \times [HOM]. \quad (8)$$

The same three loss paths were taken into account: condensation sink, dilution and wall loss. The lifetime of HOM in the chamber has been measured to be longer than for sulfuric acid (Kirkby et al., 2016).

We calculated yield terms for sCI and HOM formation in the CLOUD chamber by fitting the model to the measured concentrations. The calculated sCI yields were 22-24% for the experiments with higher SO_2 concentration and 32% for the experiment with low SO_2 concentration. These yield values are somewhat larger or in the upper end of the yield values measured in flow tube measurements in TROPOS (Sipilä et al., 2014). Sipilä et al. did their measurements in higher temperatures than we did our measurements in the CLOUD chamber. Since we use the same loss term, it can cause underestimation of the modelled sulfuric acid concentration in the CLOUD chamber which would explain this difference. For the HOM yields we got values 3.5-6.6% which are in good agreement with previously determined yields (Ehn et al., 2014; Jokinen et al., 2015; Kirkby et al., 2016) and the simulated time evolution reproduces the measured concentrations well. The simulation fitted to the data and the measured concentrations of one experiment are shown in Figure 7.

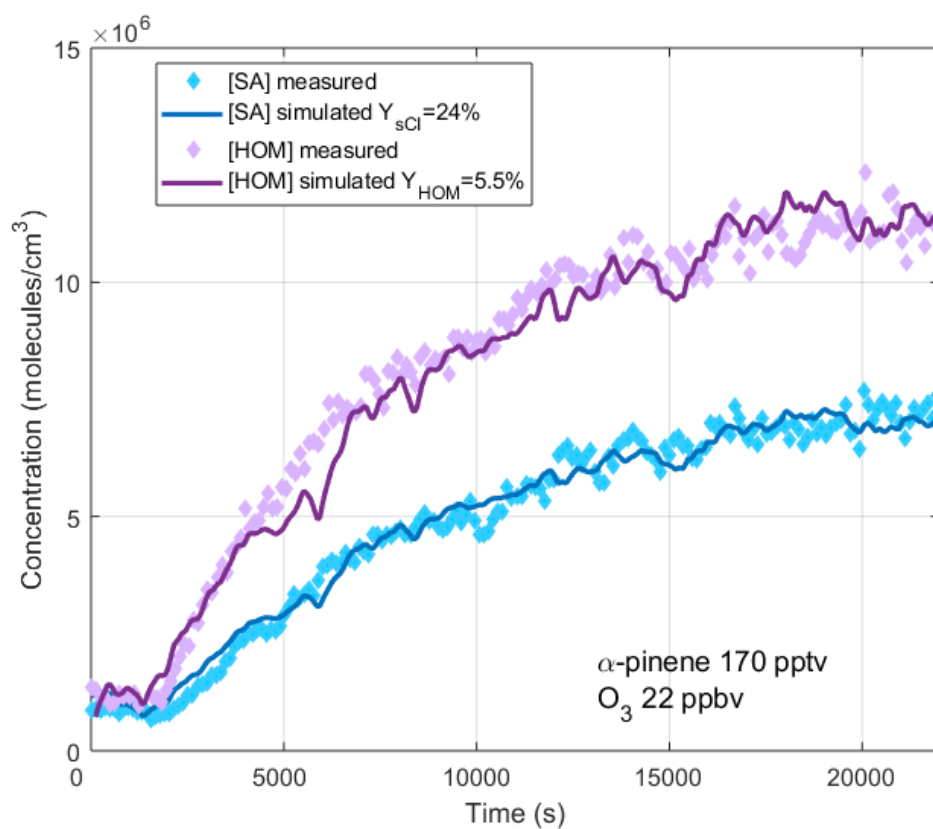


Figure 7. Example of measured and simulated concentrations of sulfuric acid (SA) and highly oxygenated molecules (HOM) in one experiment in the CLOUD chamber.

4 Field observations of condensable vapors and new particle formation

4.1 Sulfuric acid production in Boreal forest

Mauldin et al. (2012) measured sulfuric acid and OH-radical concentrations in Boreal forest and found out that during several evenings and nights the sulfuric acid concentration was remarkably high even though the OH-radical concentration was an order of magnitude lower, indicating that all of the sulfuric acid formation could not be explained by OH-radical oxidation. The concentration of unexplained sulfuric acid was measured to be up to $3 \cdot 10^6$ molecules/cm³. When they added an OH scavenger (propane) to their measurements, they were able to measure non-OH oxidants of SO₂ (X) and got concentration values of $0.3\text{--}2.0 \cdot 10^6$ molecules/cm³ for this unknown oxidant X. Because their measurement consisted of only one injection position for SO₂ that was used to determine the concentration of X, there is a possibility that some part of the measured concentration of X was produced inside the flow reactor. That is why we developed a new flow reactor with four SO₂ injectors to enable measurements of both concentration and production rate of X (section 2.2, **Paper I**). We conducted measurements at SMEAR II station and measured concentrations of $0.5\text{--}8.0 \cdot 10^5$ molecules/cm³, which is in reasonable agreement with previously measured concentrations at the same site. Berresheim et al. (2014) measured similar X concentrations of $0.4\text{--}1.6 \cdot 10^6$ molecules/cm³ in coastal area, in Ireland. The concentrations measured in the Boreal forest were unexpectedly high, since in previous studies the sCI concentration has been estimated to be significantly lower ($2 \cdot 10^4$ molecules/cm³) in rural areas whereas the concentration in polluted areas was expected to be same order of magnitude than our results (Vereecken et al., 2012; Welz et al., 2012).

To gain more insight into the sulfuric acid formation in the conditions of Boreal forest, we calculated a one day example of production of sulfuric acid from OH and sCI oxidation pathways (Figure 8.). For the calculation we used typical springtime and summertime concentrations of precursors (OH, O₃, SO₂, C₁₀H₁₆) and condensation sink measured in SMEAR II station (Kulmala et al., 2001; Rinne et al., 2005; Junninen et al., 2009; Petäjä et al., 2009). We used Y_{sCI} term of 22% derived from CLOUD measurements (**Paper III**). The results show how during the daytime the OH oxidation pathway dominates but during night time both oxidation pathways are important. In these calculations only the sCI formed from monoterpenes were taken into account so the sCI coming from other alkenes could complement the sCI pathway.

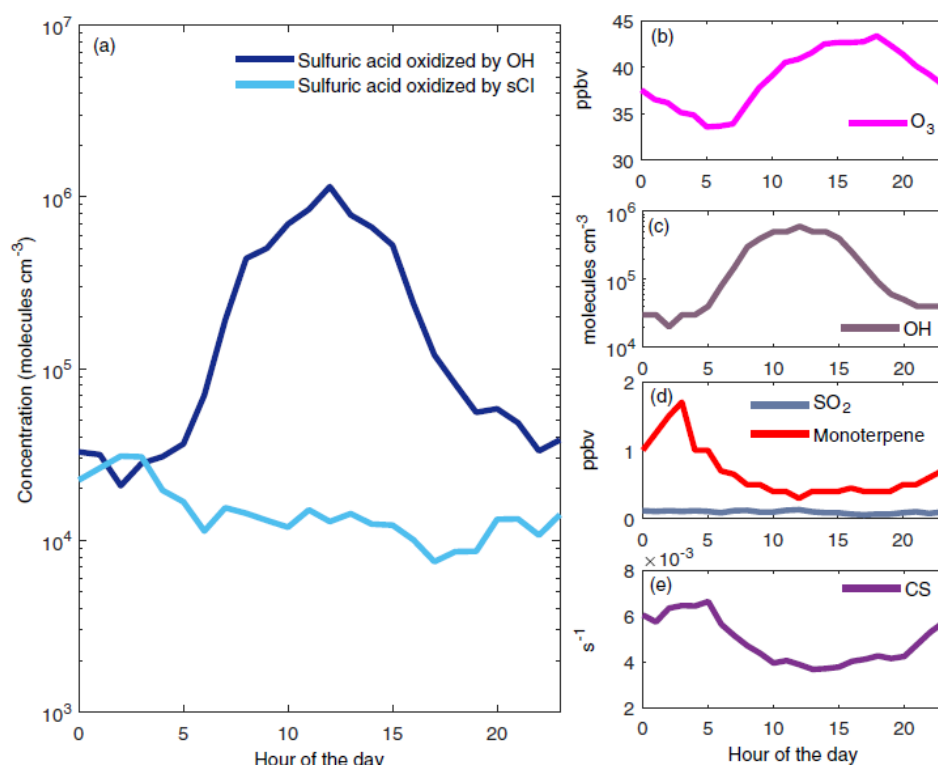


Figure 8. Example of sulfuric acid concentration produced by OH and sCI in ambient boreal forest conditions (a), their precursors (b-d) and condensation sink (e). Figure from **Paper III**.

4.2 Dimethylamine and other bases in Boreal forest

As dimethylamine was seen to enhance the particle growth significantly due to its ability to stabilize the sulfuric acid clusters (Petäjä et al., 2011; Paasonen et al., 2012; Almeida et al., 2013), we wanted to study the dimethylamine concentrations in the Boreal forest during spring time when the new particle formation is detected most frequently (40-50% of the days according to Nieminen et al. (2014)). Two studies have measured the dimethylamine concentrations in SMEAR II station previously and their results differ: Schobesberger et al. (2015) estimates that the dimethylamine concentration stays below 1 pptV according to their APi-TOF measurements whereas Kieloaho et al. (2013) measured dimethylamine concentrations with filters measured with liquid chromatography electrospray ionization mass spectrometry and got average concentration of 42.2 pptV. In the APi-TOF measurements at the site, most of the detected molecular clusters consisted sulfuric acid and ammonia rather than sulfuric acid and dimethylamine during new particle formation events. This indicates that ammonia is more important in particle formation in Boreal forest site (Schobesberger et al., 2015).

In our measurements with bisulfate-cluster-CI-APi-TOF we found out that the concentration of dimethylamine was below 150 ppqV during the whole measurement period from May to June 2013 (**Paper II**). In the light of these results, dimethylamine does not seem to have big

role in particle formation in the Boreal forest, at least in Hyytiälä. We detected trimethylamine (or its isotope propylamine) with a higher signal than dimethylamine and if we used the calibration coefficient of dimethylamine, we could estimate the concentration of it to be few tens or hundreds of ppqV. At the same time, we measured ammonia concentrations with an average of 610 pptV but since our ammonia calibration has significant uncertainty, this number is also subject to large uncertainty of at least a factor of five. Nevertheless, we can say that the ammonia concentrations were significantly higher than the dimethylamine concentrations, and our results are in good agreement with the study of Schobesberger et al. (2015) showing that ammonia has larger role than amines in the new particle formation in the Boreal forest.

4.3 Condensable vapors and particle production in the vicinity of an oil refinery

As the neutral sulfuric acid-dimethylamine clusters had been detected in chamber measurements (Kürten et al., 2014), but not in the ambient measurements in the Boreal forest (Jokinen et al., 2012), we wanted to conduct a field campaign in an environment, where the sulfuric acid concentration is presumably high, in order to study if the ambient neutral sulfuric acid clusters can be detected (**Paper IV**). We had a measurement campaign in the vicinity of an oil refinery during summertime when the sulfur dioxide concentrations are typically the highest on the site. When the air masses were coming from the oil refinery, industrial area and non-industrial area the median sulfuric acid concentrations were $1.15 \cdot 10^7$ molecules/cm³, $4.37 \cdot 10^6$ molecules/cm³ and $1.28 \cdot 10^6$ molecules/cm³, respectively. The daily maximum concentration was above 10^7 molecules/cm³ during most of the days, which is an order of magnitude higher than in Boreal forest (Petäjä et al., 2009) and at the upper end of the concentration measured at other sites (Berresheim et al., 2002; Kuang et al., 2008; Kerminen et al., 2010; Mikkonen et al., 2011). We could calculate that 36-65% of the growth during the new particle formation events was due to sulfuric acid condensation. The contribution of sulfuric acid to growth was clearly higher than in Boreal forest where it is usually around 10% or even lower during summertime (Nieminen et al., 2014).

The sulfuric acid concentration correlated with the measured 1-2 nm particles but we did not observe sulfuric acid clusters in the mass spectrum of CI-APi-TOF. The absence of clusters can be due to low concentrations of stabilizing bases (such as ammonia and dimethylamine; their concentrations were not measured) or due to high sink of the clusters. The measurement station is surrounded by vegetation and we detected high concentrations of HOM but their correlation with the 1-2 nm particles was not significant. It is also possible that the molecular clusters consisted of sulfuric acid and various HOM so that they were distributed on a wide mass range and were not detected due their low concentration.

4.4 Iodic acid driven particle formation

Iodine oxides have been connected to particle formation over coastal areas (O'Dowd et al., 2002b; O'Dowd and de Leeuw, 2007; McFiggans et al., 2010; Mahajan et al., 2011) but until recently there have not been tools to resolve the molecular-level formation pathways of ambient iodine clusters. Hoffmann et al. (2001) made laboratory experiments of ozonolysis of CH_2I_2 that caused rapid formation of particles. Chemical characterization of those particles showed that they consisted purely of iodic oxides. The high iodine emissions have been associated with low tide which results to exposure of seabed algae to ambient air. During these iodine emissions strong bursts of new particles are detected on the site with high total concentration of particles ($>10^5 \text{ cm}^{-3}$, O'Dowd et al., 2002a).

In **Paper V** we describe the first measurements of iodine-driven particle formation with CI-API-TOF. During our campaign, we observed several “apple” type new particle formation events (Figure 9A) where we observed vast amount of particles sized between 1.5 and 10 nm. During the “apple” type events only particles of certain size are detected because the source of condensing vapors is limited to a relatively small area close to the measurement site (Dal Maso et al., 2002; Ehn et al., 2010b). Simultaneously measured vapor concentrations show that some hours before the event the iodic acid concentration starts to increase and during the event the concentration is above $10^8 \text{ molecules/cm}^3$ while sulfuric acid concentration is almost two orders of magnitude lower (Figure 9B). At the same time that we detect high concentration of particles, we detect iodine oxide clusters with mass/charge ratio up to 2200 m/z.

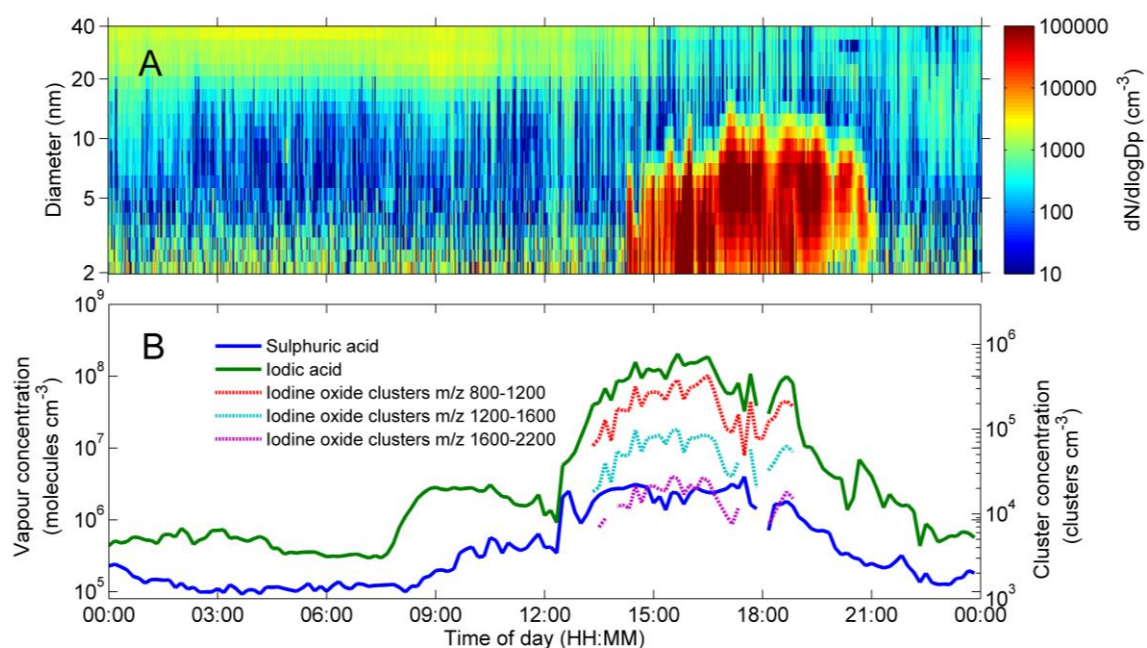


Figure 9. An example of “apple” type particle formation event at Mace Head. **A** the particle distribution measured with NAIS and **B** the concentrations of sulfuric and iodic acid and sums of different sized iodine oxide clusters.

Further investigation of the mass spectra revealed the pathway of cluster formation (**Paper V**). The average O:I ratio of the clusters was generally 2.4, which means that simple condensation of iodine compounds that have previously thought to be essential in particle formation, such as OIO, I₂O, I₂O₄ (Hoffmann et al., 2001; Saunders et al., 2010), cannot explain the observed clusters. We observed that the clusters with the highest signals were iodic acid and its clusters that form in inclusion of second iodic acid and subsequent loss of water (R9-R10). We can follow the growth of molecular clusters with this pathway up to clusters with twelve iodic acid (Figure 10.) and calculated diameter size of approximately 1.1 nm assuming the density of I₂O₅ (4.98 g cm⁻³) as follows:



In addition to clusters with elemental composition of (I₂O₅)_n(HIO₃)_m, we detected large amount of other iodic oxide clusters with lower signal intensities. These clusters had similar composition but their oxygenation level varied. The less oxygenated clusters might be due to influence of other iodine oxoacid such as HIO₂ or HIO. We detected HIO₂ and HIO during the event but with two orders of magnitude lower concentration than iodic acid. Some of the observed clusters had also sulfuric acid, nitric acid or ammonia in them but the vast majority of them were pure iodine oxide clusters.

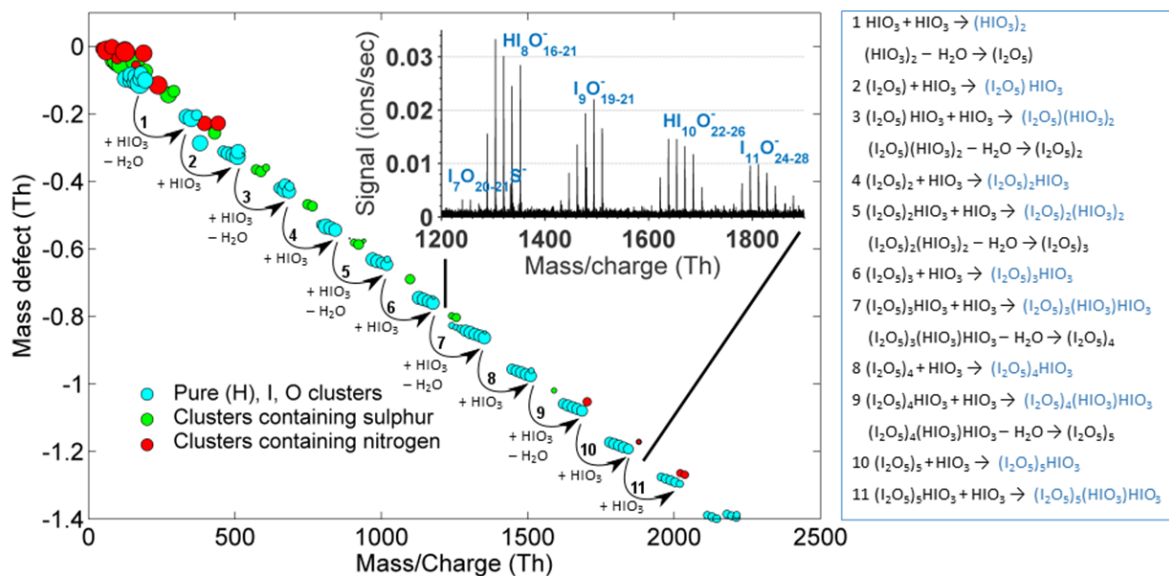


Figure 10. Mass defect versus cluster mass during a particle formation event in Mace Head. Mass defect is the difference of the exact mass of the cluster from its nominal mass (i. e. sum of its neutrons and protons). The area of the dots is proportional to the observed signal. On the right hand side, the molecular clustering pathway is presented and the observed clusters are shown in blue.

The occurrence of iodic acid is not limited to coastal areas with macro algae. We have studied two sites, one from high Arctic and one from Antarctica, where we have detected elevated concentrations of iodic acid (**Paper V**). In coastal site of Northern Greenland, we

observed new particle formation driven by iodic acid. During the events, the iodic acid concentration was approximately order of magnitude lower than in Mace Head and the particle concentrations were significantly lower. Interestingly the clusters observed in the high Arctic had elemental composition of $(\text{I}_2\text{O}_5)_n(\text{HIO}_3)_m$, thus, they were the same that had the highest signal intensities in Mace Head. In the Arctic conditions with significantly less iodic acid, it seems that only the most abundant clusters were above our detection limit. The measurement site in the Antarctica was more than 100 km from the coast but we were able to observe clear signal of iodic acid also there. The iodic acid concentration was two orders of magnitude lower than in Mace Head and in these conditions we did not observe particle formation driven by iodic acid.

5 Review of papers and the author's contribution

Paper I describes a new instrument for measuring atmospheric concentrations of non-OH oxidants of SO₂. We developed a new instrument by connecting a flow reactor with a chemical ionization inlet used with API-TOF. In the paper we explain the performance of this new instrument and show results of the first ambient measurements with it. The measurements were conducted in Boreal forest at Hyytiälä SMEAR II station. I did the laboratory and field measurements with colleagues. I did the mass spectrometry data analysis and contributed in writing the paper.

Paper II describes a new instrument to measure bases that can stabilize sulfuric acid clusters such as amine and ammonia. In the paper we explain the performance of the new instrument and present results from the first ambient measurements of it at SMEAR II station. I conducted the laboratory measurements and the field measurements with colleagues, analyzed the data and participated in writing the paper.

Paper III presents measurement-model comparison of stabilized Criegee intermediate and highly oxygenated molecule production in the CLOUD chamber. In this study we continued the study of non-OH oxidants of SO₂ by conducting experiments in the CLOUD chamber and modelling the formation of sulfuric acid. We also studied concurrently the formation of HOM from α -pinene oxidation. I conducted the measurements in CERN with colleagues, I did the data analysis, model comparisons and wrote the paper.

Paper IV presents in-situ observations of trace gases, aerosol particles and their precursors measured in the vicinity of an oil refinery. In the study we focus on the production of sulfuric acid and particulate matter but also detected HOM and their precursors. I was responsible of conducting the measurement campaign, analyzed most of the data and wrote the paper.

Paper V introduces a new chemical pathway to form aerosol particles via sequential addition of iodic acid. In this study we measured particle formation events in the coastal site of Mace Head research station and managed to observe particle formation in molecular level for the first time in ambient measurements. I did the measurements with colleagues, analyzed the mass spectrometry data and participated in writing the paper. In the paper we also utilized data from Arctic and Antarctic stations. I conducted the Arctic measurement campaign with colleagues and analyzed the data.

6 Conclusions

In this thesis, we widened the understanding of the first steps of new particle formation by using new mass spectrometric methods to measure the key condensable vapors: sulfuric acid, dimethylamine, highly oxygenated molecules, iodic acid and its clusters, and combined the chemical measurements with particle measurements. We also developed an indirect method to measure an atmospherically relevant oxidizer: stabilized Criegee intermediate. We studied the new particle formation in several field measurements and extended our understanding by conducting chamber experiments with the same precursors observed in the field studies. In addition, we used kinetic model to further comprehend the formation of condensable vapors.

The knowledge of the role of sCI in the sulfuric acid formation has been lacking measurement in ambient conditions. In this thesis we enhanced our knowledge by two studies: we measured pure sCI oxidation of SO₂ in the CLOUD chamber and used experimental parameters derived from flow tube measurements to simulate the sulfuric acid formation (**Paper III**) and we developed a new field-deployable instrument to measure the sCI and other non-OH oxidants of SO₂ (X) (**Paper I**). We found molar yields in the range of 22-32 % for the formation of stabilized Criegee intermediates by fitting our model to the measured concentrations. These values are on the upper edge or above of the values published before (Sipilä et al., 2014) and there is a need for more experimental work to clarify the parameters affecting sCI formation. The first measurements of X-oxidant in the Boreal forest with FR-CI-APi-TOF yielded similar concentrations that was measured before convincing that also the previous measurements with only one injector were valid (Mauldin et al., 2012).

While we studied the formation of sCI in the CLOUD chamber we also followed the formation of HOM by ozonolysis of α -pinene (**Paper III**). We managed to simulate the formation of highly oxygenated molecules very well with our model and we calculated molar yields of 3.5-6.5 % which are in the same range than previously published yields (Ehn et al., 2014; Jokinen et al., 2015; Kirkby et al., 2016).

Although the importance of ammonia and amines, even at minute concentrations, has been noted lately, there has not been any method to detect them at critical sub-pptV concentration range. In **Paper II** we developed a mass spectrometric method to measure dimethylamine with concentrations down to 70 ppqV in chamber measurements and 150 ppqV in ambient measurements. Further calibrations are needed to determine the sensitivity towards other amines and ammonia. In our measurements in the Boreal forest, we observed significantly higher concentration of ammonia than amines and the concentration of dimethylamine was under our detection limit during the whole measurement period. According to these results, dimethylamine does not seem to have a large role in particle formation in the Boreal forest, at least in Hyytiälä. Hemmilä et al. (2018) measured amine concentrations with online ion-chromatograph coupled with mass spectrometry and ammonia concentrations with online ion-chromatograph at SMEAR II station few years after us and measured significantly

higher DMA concentrations and lower ammonia concentrations compared to our measurements. One possible reason for that is that while we measure only gaseous bases, the ion-chromatograph might also include small molecular clusters into its total concentration. Recent ammonia and amine measurements in Boreal forest have shown significant variation in concentration levels (**Paper II**, Kieloaho et al., 2013; Schobesberger et al., 2015; Hemmilä et al., 2018). Simultaneous measurements of these different measurement techniques would be crucial to understand which amount of the variation is due variation of base emissions during different years and which amount is due differences in instrumental sensitivities.

In spite of comprehensive field measurements even in conditions with high sulfuric acid concentrations (**Paper IV**) we did not yet measure neutral molecular clusters of sulfuric acid or organic compounds in the atmosphere. There could be several reasons for that: 1) lack of stabilizing compounds, 2) fragmentation in the mass spectrometer or 3) concentration below our detection limit. Sulfuric acid clusters need strong stabilizing agents for making them stable enough to be measured and according to our measurements the base concentrations are extremely low for example in Boreal forest potentially explaining the apparent lack of sulfuric acid clusters there. The fragmentation in the mass spectrometer is not yet well characterized but since plenty of molecular clusters have been detected in APi-TOF measurements and the conditions inside the mass spectrometer are the same, they should be measurable also with CI-API-TOF. There are hundreds of different HOM and often there is not any single compound standing out but their concentration is divided over a large mass range. As a result, also the molecular clusters containing HOM are divided into wide mass range and it is likely that none of them is crossing the detection limit by itself.

In the **Paper V** we managed to give more insight in the iodine-driven particle formation. We were able to follow the molecular cluster formation molecule by molecule and proposed that the cluster formation primary proceeds by sequential addition of iodic acid followed by intracluster restructuring to I_2O_5 and removal of water. Our study also showed how the iodine-driven particle formation is not limited to only scarce coastal areas close to macro algae beds but similar particle formation happens also in the Arctic environment surrounded by sea ice.

In the introduction of this thesis, we specified three main objectives for it. The first objective was to develop new measurement techniques and it was fulfilled by **Papers I-II**, in which we developed techniques for determining the concentrations of stabilized Criegee intermediates and atmospheric bases utilizing nitrate-ion chemical ionization mass spectrometry. Both of the new measurement techniques were tested in laboratories and in field measurements at the SMEAR II station. The second objective was to investigate the formation of HOM and the oxidation of sulfur dioxide purely by stabilized Criegee intermediates in controlled chamber conditions with ozone and α -pinene and it was carried out in **Paper III**. We compared the measured concentrations of vapors against a kinetic model results and the simulated time evolution reproduced the measured concentrations well. The simulated and measured concentrations of HOM were especially uniform but sulfuric acid formation showed more discrepancy. The third goal was to identify the

condensable vapors and molecular cluster formation pathways of new particle formation in different kind of environments and that we have shown in **Papers I-II** and **IV-V**. As a key finding, we identified of the role of iodic acid in cluster formation and presented its occurrence in several environments. In addition, we found out that dimethylamine did not play a significant role in the particle formation in Boreal forest during our measurement period and that sulfuric acid had significant contribution to the growth of nanoparticles in the vicinity of an oil refinery.

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